

# Damage mechanism of polyphenylene sulfide resin in liquid oxygen

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Received: 22 June 2011 / Accepted: 17 December 2011 / Published online: 19 January 2012  
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**Abstract** A compatible material is defined as one that maintains its original properties in the presence of liquid oxygen. A test for the compatibility of a material with liquid oxygen basically consists of placing the material in liquid oxygen in the presence of a possible ignition source and observing the reaction as a function of the ignition energy. One of the most probable ignition sources is just mechanical impact and in an appropriate test, the disk of a candidate material is submerged in liquid oxygen and impacted with 98 J of impact energy while monitoring a candidate material for flash or sound responses that would correspond to an ignition. The polyphenylene sulfide resin was mechanically impacted in liquid oxygen according to ASTM D-2512 to investigate the compatibility and damage mechanism. The obvious flash was detected for three specimens during the initial series of 20 tests, which demonstrated that the polyphenylene sulfide resin is incompatible with liquid oxygen. The surface microstructure and composition of the specimen before and after mechanical impact were analyzed by SEM and XPS, respectively. The damage mechanism of the polyphenylene sulfide resin in the liquid oxygen was investigated in detail. The high temperature of the local surface resulted in the reaction of polyphenylene sulfide resin with oxygen in forming peroxy radicals of relatively high activity which reacted with hydrogen atoms of polyphenylene sulfide of molecular terminals producing relatively stable sulfur radicals and peroxides. The disappearance of radical of high activity is

favorable to inhibit the reaction of the polyphenylene sulfide resin with liquid oxygen.

**Keywords** Damage zone · Degradation · Diffusion · Structure

## Introduction

The liquid oxygen has been used widely in many different applications ranging from conventional industry to high-technology industry, such as seals, lubricants, filling liquids, and so on [1]. During its production, transport and use, the liquid oxygen is in contact with many different materials, virtually all of which would burn [2]. The problem of choosing properly safe or compatible materials is the objective of presenting a brief survey of the compatibility of structural materials with liquid oxygen [3]. A compatible material is defined as one that maintains its original properties in the presence of liquid oxygen. The oxidation process of bulk materials is either very slow and controllable or violently fast and destructive; incompatibility is generally analogous to the latter. A test for the compatibility of a material with liquid oxygen basically consists of placing the material in liquid oxygen in the presence of a possible ignition source and observing the reaction as a function of the ignition energy [4]. The test is only distinguished by the ingenuity of selecting possible ignition sources. However, the type of test is quite important in simulating working conditions and probable ignition sources. Somewhat arbitrarily, the test is described below by the following ignition categories: mechanical impact, electrical, thermal, acoustic, abrasive, fracture and configurational [5]. The mechanical impact as one of the most probable ignition sources is conducted by submerging a disk of a candidate material in liquid

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oxygen and impacting it with an impact energy of 98 J while monitoring the material for signs of flash or sound responses that would correspond to an ignition [6]. Strictly speaking, these are not compatibility tests, but do provide a basis for understanding the potential chemical reactions.

The polymer matrix composites have been used widely in many aerospace applications, which are especially true for space applications where the payoff from weight savings is typically highest [7–9]. The current re-useable launch vehicle calls for propellant tanks carrying liquid hydrogen or liquid oxygen. If polymer matrix composites are to replace metals as the tank material, it is estimated that the total tank weight can be reduced by as much as 27–35% [10]. However, most polymer matrix composites may ignite or initiate reactions when in contact with liquid oxygen if they are subjected to mechanical impact. The polyphenylene sulfide resin is an attractive matrix material because of its excellent mechanical properties, high temperature durability, chemical resistance and easy processing. For flight safety, the liquid oxygen compatibility of the polyphenylene sulfide resin must be characterized to define the degree of hazard associated with their use in an oxygen-rich environment and handling procedures. Furthermore, with the development of China's space program, it is necessary to investigate the liquid oxygen compatibility of polymer matrix composite to enhance carrying capacity of the aircraft, and the liquid oxygen compatibility is in substance oxidation reaction related to oxygen diffusion, physical and chemical properties of polymer matrix composites, such as bond energy and functional group. The investigation on the liquid oxygen compatibility of polymer matrix composite is favorable to explore the mechanism of reaction of polymer with oxygen and the aging of polymer matrix composite. Nevertheless, the research on the compatibility of polymer matrix composites with liquid oxygen is rare and scattered; especially the damage mechanism of the polymer matrix in liquid oxygen is not reported in open literature.

In the present work, the polyphenylene sulfide resin was mechanically impacted in liquid oxygen to estimate the liquid oxygen compatibility of the polyphenylene sulfide resin according to ASTM D-2512. The surface microstructure and composition of the polyphenylene sulfide resin before and after mechanical impact were investigated and analyzed in detail to investigate the damage mechanism of the polyphenylene sulfide resin in liquid oxygen.

## Experimental

### Materials

The hydrogen sulfide ( $\text{H}_2\text{S}$ ), sodium hydroxide ( $\text{NaOH}$ ) and *p*-dichlorobenzene (*p*-DCB) were used as raw materials, and sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) was used as an

assistant. These analytically pure raw materials were purchased from Tianli Chemical Reagent Co. (China).

### Polymer preparation

The polyphenylene sulfide resin was synthesized for 4–6 h under normal pressure in hexamethylphosphoryltri-*n*-butylamide (HPTA). The polyphenylene sulfide resin was repetitiously refined to 99.0%.

### Polymer tests

The liquid oxygen compatibility of the polyphenylene sulfide resin was determined under impact energy using the Army Ballistic Missile Agency (ABMA)-type impact tester, as described in ASTM D2512-95(2008) [11].

A specimen of a test material was placed in a specimen cup, pre-cooled and covered with liquid oxygen for 5 min, and placed in the cup holder located in the anvil region assembly of the impact tester. A pre-cooled striker pin was then centered in the cup. The plummet was dropped from selected heights onto the pin, which transmitted the energy to the test specimen. Observation for any reaction was made and the liquid oxygen impact sensitivity of the test material was noted. Drop tests were continued using a fresh specimen cup and striker pin for each drop, until the threshold value was achieved. A series of drop tests were conducted at an energy level of 98 J or as specified for the pass/fail tests. This test method could also be used for acceptance of testing materials in liquid oxygen systems. Twenty separate samples of the material submerged in liquid oxygen were subjected to 98 J (72 ft-lbf) or as specified and the impact energy was delivered through a 12.7 mm (1/2 in.) diameter contact. More than one indication of sensitivity would be a cause for immediate rejection.

A single explosion, flash, or other indications of sensitivity during the initial series of 20 tests require that an additional 40 samples must be tested with no incident to ensure acceptability of the material.

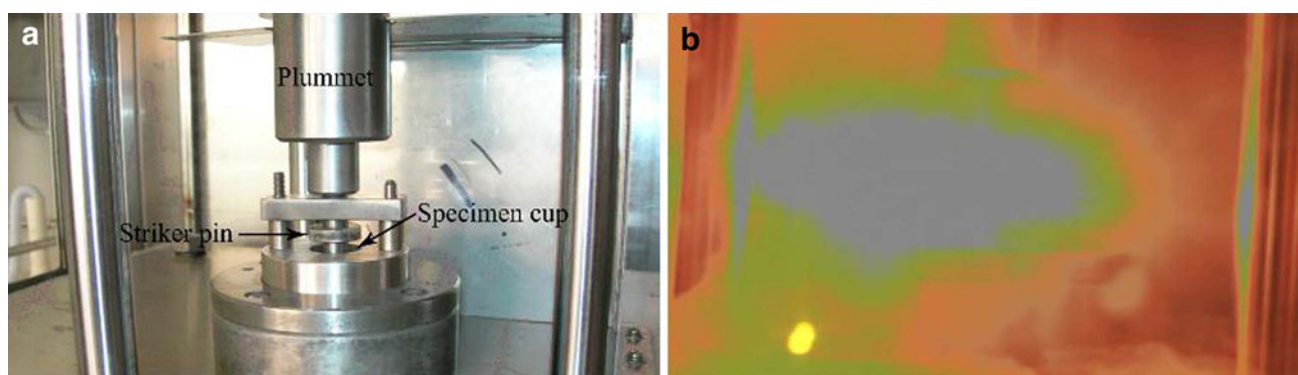
The surface element compositions of the resin were measured using the X-ray photoelectron spectroscopy (XPS) along with an X-ray photoelectron spectrometer (Perkin-Elmer, PHI 5300) equipped with magnesium X-ray source. The microstructural features of the specimen were observed by scanning electron microscopy (SEM, FEI Sirion, Holland) with simultaneous chemical analysis by energy dispersive spectroscopy (EDS, EDAX, Inc).

## Results and discussion

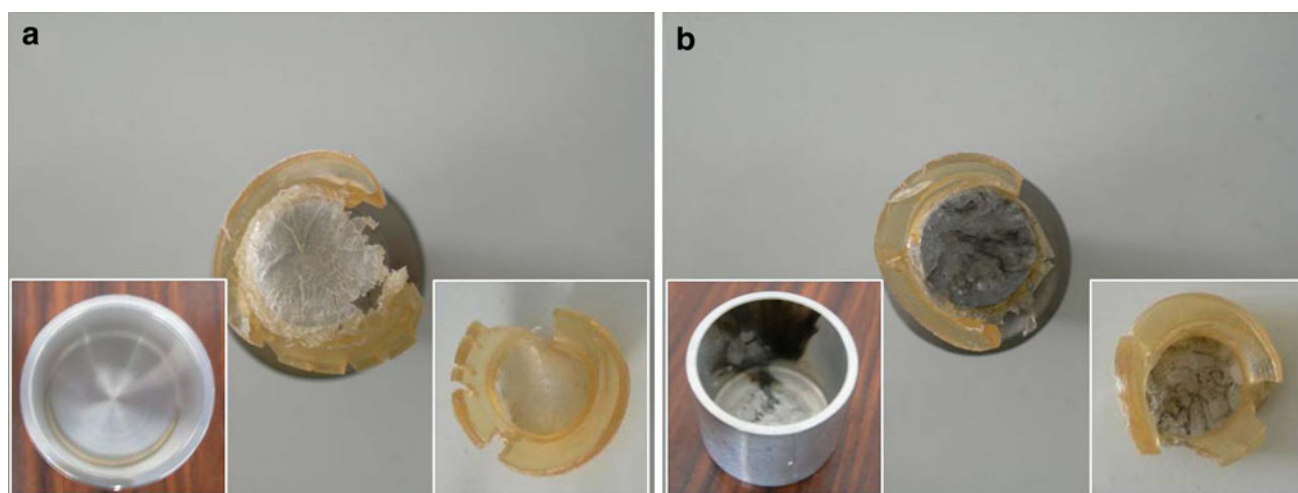
### Experimental results and microstructure

Figure 1a shows a macrograph of the impact tester and the plummet moving 1.0 m upwards when the experiment





**Fig. 1** The photo of the impact tester (a) and the video screenshot (b) of the individual specimen in the process of impact



**Fig. 2** The photo of the impacted specimen without (a) and with (b) flash during impact

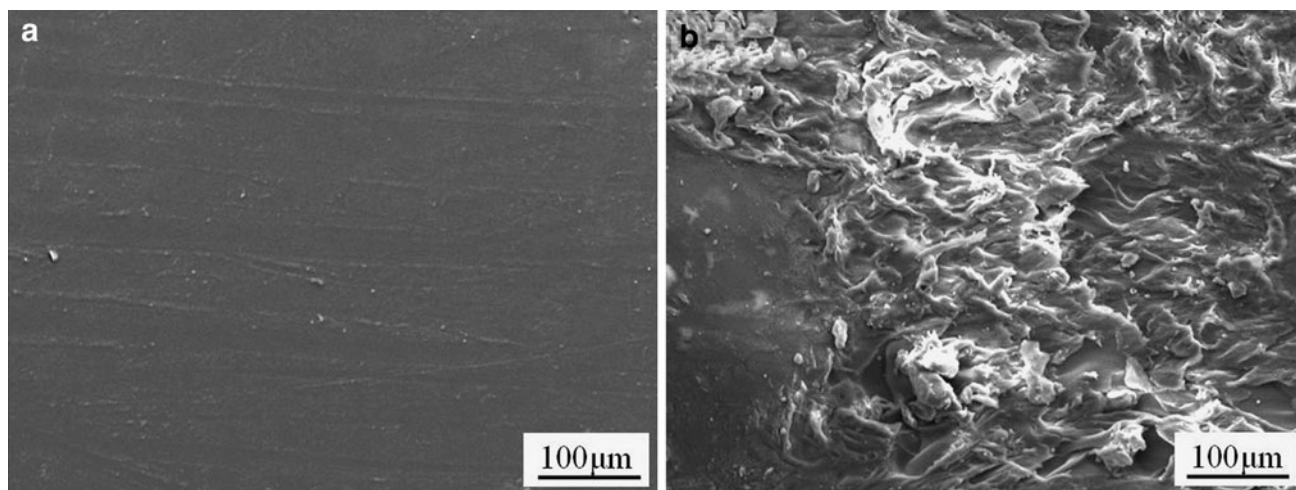
begins. This tester is designed to allow a plummet to make approximately a free fall on top of a striker pin, the bottom of which is in contact with the specimen immersed in liquid oxygen. A Vidicon device has been used to record the flash generated due to temperature rise during impact and the instantaneous video screen-shot of the individual specimen in the process of impact shown in Fig. 1b. The obvious flash was detected for three specimens during the initial series of 20 tests, which indicated that the polyphenylene sulfide resin is incompatible with liquid oxygen.

The macrograph of the impacted specimen without flash during impact is shown in Fig. 2a. The obvious deformation of the impacted specimen which was observed due to mechanical impact and a large number of cracks occurring in the deformation region seemed favorable to consume the impact energy of the plummet. The interior of the specimen cup was clean and the color of the specimen cup was changed compared with the specimen cup before impact. Figure 2b shows the macrograph of the impacted specimen with flash during mechanical impact and the black besmoke on the sidewall of specimen cup which was readily detected due to the incomplete combustion of the

polyphenylene sulfide resin. The crack edge in the deformation region of the impacted specimen was covered with the black besmoke. Compared with the macrograph of the impacted specimen without flash, the macrograph of the impacted specimen with flash did not show obvious difference, although the flash was detected in the process of mechanical impact of the individual specimen. Such phenomena indicated that a small quantity of active site on the surface of the polyphenylene sulfide resin was reacted with liquid oxygen [12].

The scanning-electron microscopy was used to observe the change in the microstructure of the impacted specimen. The microstructure of the deformation region of the impacted specimen without flash during mechanical impact is shown in Fig. 3a. The deformation region of crack edge is as clean as a whistle and the obvious change in the microstructure is not observed compared with the microstructure of the specimen before the mechanical impact. Nevertheless, the striking corrugation in the deformation region of crack edge of the impacted specimen with flash during the mechanical impact was observed due to extreme reaction, such as flash, as shown in Fig. 3b.





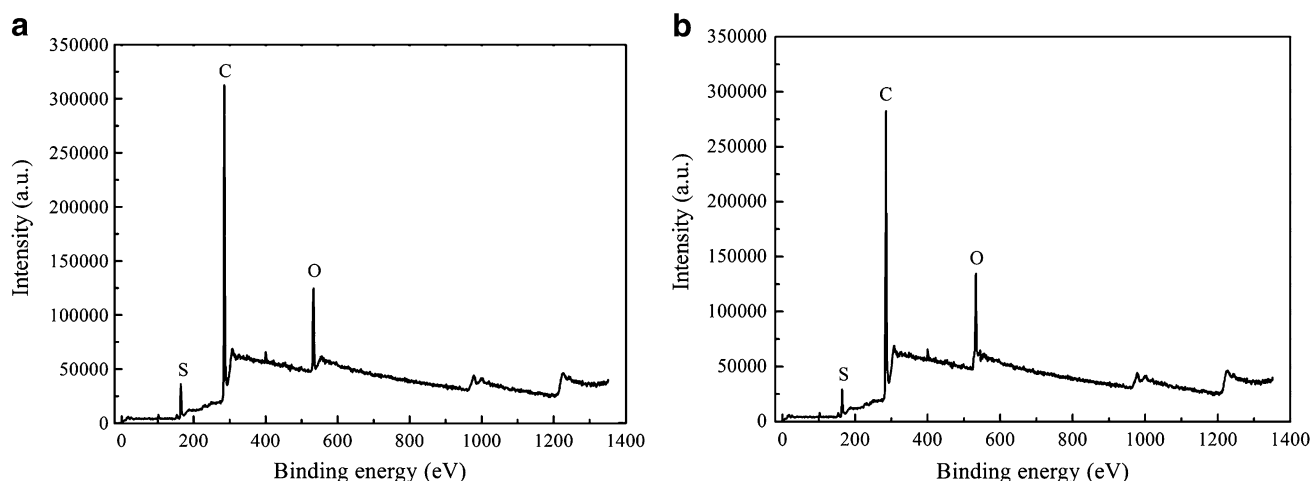
**Fig. 3** The microstructure of the deformation region of the impacted specimen without (a) and with (b) flash during impact

### Composition analyses

The overall XPS spectra of the impacted specimen with and without flash during the mechanical impact are shown in Fig. 4. There are significant differences between the impacted specimen with and without flash. The peaks of the carbon and sulfur of the impacted specimen without flash during impact are greater than that of the impacted specimen with flash during the mechanical impact. In contrast, the peak of the oxygen is lower than that of the impacted specimen with flash during the mechanical impact which reveals the significant chemical combination of oxygen with the surface of the impacted specimen with flash during the mechanical impact.

The content of the surface element of the specimen with and without flash during the mechanical impact was measured by XPS analysis and summarized in Table 1. It may be seen from Table 1 that the surface of the impacted

specimen is mainly composed of elements such as carbon, oxygen and sulfur. The contents of the carbon, oxygen and sulfur elements of the impacted specimen without flash during the mechanical impact are found to be 81.79, 12.64 and 5.51%, respectively, and the O/C ratio as 0.15. The O/C ratio as high as 0.36 for the specimen with flash during the mechanical impact has significantly increased compared with the specimen without flash during the mechanical impact due to the surface oxidation of the specimen. To confirm that the change in the surface element is actually the effect of the mechanical impact, the surface of the specimen before the mechanical impact has been analyzed by XPS and the elemental contents are also summarized in Table 1. The elemental contents of the specimen before the mechanical impact and without flash during the mechanical impact are found statistically equivalent, which indicates that the change in the surface elemental contents has been due to surface oxidation.



**Fig. 4** The overall XPS spectra of the impacted specimen without (a) and with (b) flash during impact





**Table 1** The content of the surface element of the specimen measured by XPS analysis

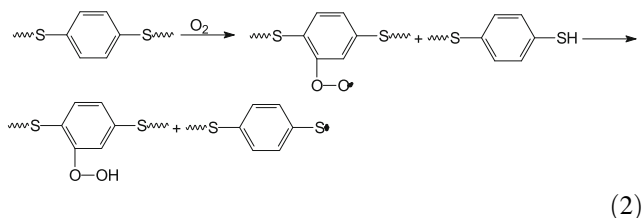
Polyphenylene sulfide	Elemental content (%)		
	C	O	S
Before	81.81	12.62	5.52
No flash	81.79	12.64	5.51
Flash	69.90	25.31	4.72

### Reaction mechanism

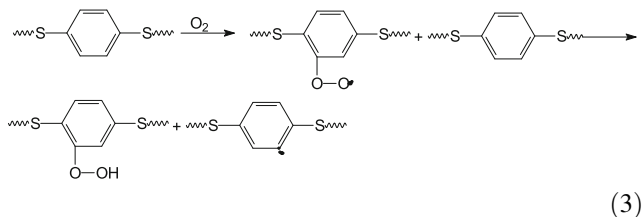
The typical molecular structure of the polyphenylene sulfide resin is shown in Eq. 1 and a lot of instantaneous energy released with the impact has resulted in temperature increase of the local surface of the specimen [1–4, 13].



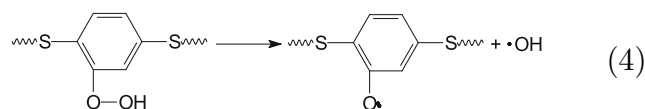
The high temperature of the local surface of the specimen resulting in the reaction between polyphenylene sulfide resin with oxygen and formation of peroxy radicals of relatively high activity which would react with hydrogen atoms of polyphenylene sulfide on the molecular terminals lead to relatively stable sulfur radicals and peroxides [14–16], as shown in Eq. 2.



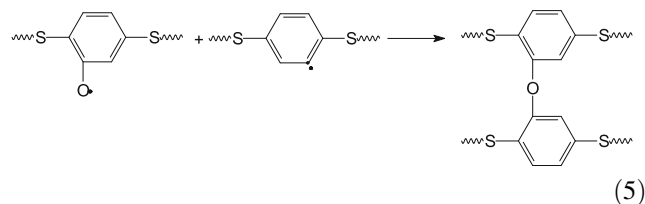
The relatively high activity of the peroxy radicals could also react with hydrogen atoms on the benzene ring of the polyphenylene sulfide which also result in relatively stable phenyl radicals and peroxides [14, 16], as shown in Eq. 3.



Furthermore, the peroxide is decomposed at high temperature producing hydroxyl radicals and phenoxyl radicals as follows:



The cross-linking reaction between polyphenylene sulfide molecules is promoted due to the reaction of the phenoxyl radicals with phenyl radicals, as shown in Eq. 5, which result in the disappearance of radical [14], which is favorable to inhibit the reaction of the polyphenylene sulfide resin with liquid oxygen.



A small quantity of impurity such as NaOH and Na<sub>3</sub>PO<sub>4</sub> is found to be present in the polyphenylene sulfide resin. However, the effect of impurity on the compatibility of the polyphenylene sulfide resin with liquid oxygen was ignored because NaOH and Na<sub>3</sub>PO<sub>4</sub> were non-flammable materials. Further work is continuing to reduce the number of active sites on the surface of the polyphenylene sulfide resin to improve the compatibility of the polyphenylene sulfide resin with liquid oxygen.

### Conclusion

The obvious flash detected for three specimens during the initial series of 20 tests was an indication that polyphenylene sulfide resin is incompatible with liquid oxygen. Compared with the macrograph of the impacted specimen without flash, the macrograph of the impacted specimen with flash did not show any obvious difference, although a flash has been detected in the process of mechanical impact test on individual specimen. Such phenomena show that a small quantity of active site on the surface of the polyphenylene sulfide resin has entered into reaction with liquid oxygen. The cross-linking reaction between polyphenylene sulfide molecules was promoted by the reaction of the phenoxyl radicals with phenyl radicals, which resulted in the disappearance of radical. The disappearance of radical is favorable to inhibit the reaction of the polyphenylene sulfide resin with liquid oxygen.

**Acknowledgments** This work was supported by China Postdoctoral Science Foundation Funded Project (20100481220) and the Fundamental Research Funds for the Central Universities (3014-852001 and DUT10ZDGO5) and the National Natural Science Foundation of China (51102031, 51002019 and 91016024).



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